Nanopatterns by Free-Standing Monolayer Films of Diblock Copolymer Micelles with in Situ Core−Corona Inversion

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Diblock copolymers composed of two different polymers, covalently linked, spontaneously self-assemble into structures on the tens of nanometer length scale, whether in bulk or in a solution.[1] For example, in a selective solvent for one of the blocks, nanometer-sized micelles consisting of a soluble corona and an insoluble core are formed above the critical micelle concentration.[2] Micelles can solubilize otherwise insoluble substances such as nanoparticles in the core.[3] In addition, these micelles can be coated onto substrates by Langmuir−Blodgett or dip-coating methods to form a variety of nanostructures, which have tremendous potential for applications in nanotechnology.[4−11]

In this Communication, we report a transferable nanopattern from a free-standing micellar monolayer film of diblock copolymers by simple spin coating. It was also possible to switch nanopatterns by core−corona inversion of micelles in situ. With this novelty, we were able to change the location of nanoparticles from isolated islands to a continuous matrix.

For a free-standing monolayer film of diblock copolymer micelles, we first prepared micellar solutions by dissolving monodisperse polystyrene-*block*-poly(4-vinylpyridine), PS−P4VP ($M_n^{PS} = 21.4$ kg/mol, $M_n^{P4VP} = 20.7$ kg/mol) in toluene to yield solutions of above 0.3 wt %. Since toluene is a selective solvent for the PS block, spherical micelles of a PS corona and a P4VP core were formed at the concentrations studied, which were well above the critical micelle concentration.[12] A film of micelles was then fabricated simply by spin coating from these toluene solutions on a piece of freshly cleaved mica. After evacuating residual solvents, the film was easily separated from the mica substrate by floating on water due to the strong affinity of water to mica. Films spin-coated from solutions of less than 0.4 wt % were finely split on the water surface, like oil on water. However, when more concentrated solutions were used, films of PS−P4VP micelles were mechanically stable as a whole piece on the water surface. Such a film was transferable to a regular TEM copper grid having no supports. That is, the film was maintained as a free-standing film without a substrate. Thus, the film can be transferred onto various substrates and be stacked by multiple transferring. Particularly, when a 0.5 wt % toluene solution of PS−P4VP was used, a free-standing film of a complete monolayer of micelles was obtained as shown in Figure 1. The film thickness measured on the substrate (ca. 29 nm) was almost identical to the micelle size, implying a micellar monolayer film. Variation of spinning speeds from 1500 to 4000 rpm showed a minor effect on the formation of a free-standing monolayer film. Faster spinning speeds generated slightly thinner monolayer films. However, solutions with higher concentrations of PS−P4VP resulted in irregularly interconnected domains of an additional layer on the monolayer, which were also reported in the case of dip coating of micellar solutions.[13,14] Transformation of spherical to wormlike micelles reported in dip coating at high concentrations[5,6,14] was not observed in our case, probably because the spin-coating procedure produces a kinetically frozen phase by very rapid solvent evaporation.

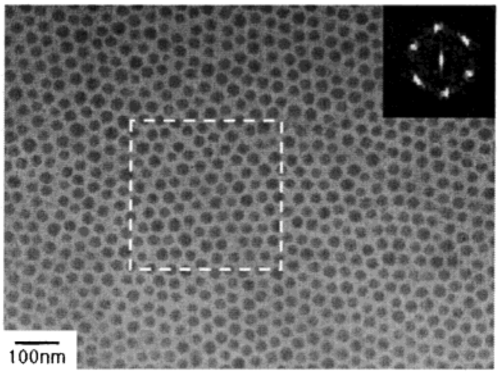

Figure 1. Plan-view TEM image of a free-standing monolayer film of PS−P4VP micelles. The P4VP block was selectively stained with I_2 and appeared as dark spherical cores. Inserted is a Fourier transformed pattern of the boxed area.

Figure 1 is a representative internal structure of a free-standing film of a complete monolayer of PS−P4VP micelles fabricated with a 0.5 wt % solution at 2000 rpm. For the contrast in transmission electron microscopy (TEM), the P4VP core was selectively stained by I_2 vapor and appeared as dark spheres in the image. To a certain extent, the staining procedure could expand the P4VP core. As shown in Figure 1, the film was definitely a monolayer of micelles, made up of a continuous bright PS matrix and dark spherical P4VP cores with short-range hexagonal packing, confirmed by a Fourier transformed pattern of the boxed area. The image of Figure 1 is similar to the one reported in dip coating on substrates with a high pulling rate of a substrate, although micelles in this figure were more closely packed.[11,12] In the dip-coating case, it was reported that a faster pulling rate of a substrate produced a better coverage of micelles on the substrate.[11,12] Thus, spin coating, an extremely fast solvent evaporation case, could enhance better formation of a two-dimensionally compact monolayer of micelles. This compact monolayer of micelles made it possible to form a free-standing film, presumably by some entanglements of PS coronas.

Both surfaces of the free-standing film generated by spin coating did not show particular patterns in atomic force microscopy (AFM) images, although the surface at the air interface (rms roughness 1.2 nm) was rougher than the other surface originally at the mica interface (rms roughness 0.3 nm). In lateral force

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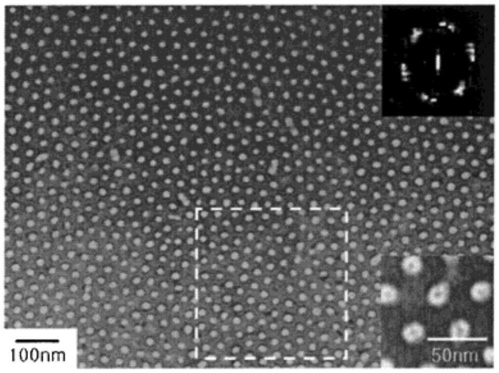

Figure 2. Plan-view TEM image of a free-standing monolayer film of PS−P4VP micelles after in situ core−corona inversion. The P4VP block was again selectively stained with I_2 and appeared as a dark continuous matrix. Images of incomplete inversion and a Fourier transformed pattern of the boxed area are inserted at the lower and the upper right sides, respectively.

microscopy (LMF) images of both sides, no specific pattern was found, implying that both surfaces were covered by the same component, presumably the PS block.

By simple dipping of this free-standing monolayer film of PS−P4VP micelles in ethanol, a selective solvent for the P4VP core, core−corona inversion was induced in situ without ruining the film. In Figure 2, we clearly observed an inverted nanopattern of micelles consisting of bright isolated PS cores and dark continuous P4VP coronas, of completely reversed contrast compared to the image in Figure 1. The short-range hexagonal packing was still maintained after inversion, which was verified again by a Fourier transformed pattern of the boxed area. The intermicellar spacing was slightly smaller than that before inversion, although there is some uncertainty because of swelling of P4VP blocks due to I_2 staining. The same in situ inversion was also possible with the film on carbon-coated TEM grids. When the dipping time of a free-standing film in ethanol was longer than 3 min, the film became deteriorated. Even a very short dipping time (less than 30 s) was enough to induce the core−corona inversion. But the inversion in a certain area was incomplete, so that a donut-type PS core having a dark inner P4VP core was produced, as shown at the lower right side in Figure 2. Both surfaces after inversion became rougher (rms roughness 2.0 nm) in AFM measurements but did not show particular patterns in LFM images, implying the same component, presumably the P4VP block on both surfaces.

Since symmetric PS−P4VP diblock copolymers were used, their micelles in solid films before or after inversion could be far from the equilibrium and could be considered as kinetically frozen structures by rapid solvent evaporation. Thus, the selective solvent for the core block could effectively reorganize the core and corona of micelles in a relatively short period without long-range diffusions of the copolymer, which may result in film deterioration. In addition, there can be the possibility that the cores of micelles simply swell by ethanol and ultimately touch and coalesce to form the inversed nanopattern. It was also possible to re-invert the core to the corona by using toluene, a selective solvent for the PS block, i.e., back to Figure 1 from Figure 2. But reversibility was limited because a packing of micelles became poor and deteriorated.

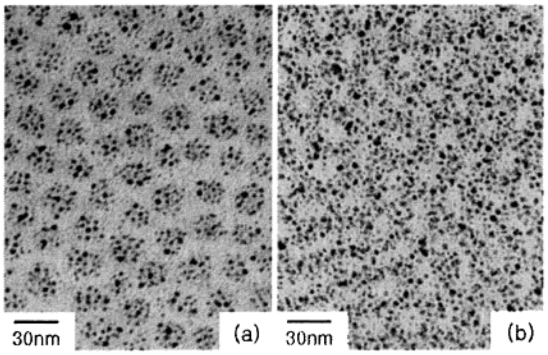

Figure 3. Plan-view TEM images of monolayer films of PS−P4VP micelles containing electron-beam-reduced silver nanoparticles (a) before and (b) after in situ core−corona inversion.

We applied this in situ core−corona inversion of micelles to nanoparticle synthesis. A variety of metal salts, precursors of nanoparticles, can be selectively coordinated to the P4VP block.[3] As a representative example, silver acetate (AgAc), was dissolved in a 0.5 wt % PS−P4VP toluene solution (molar ratio of AgAc/4VP = 0.5), and a free-standing film from this solution was fabricated, and then in situ core−corona inversion in the film was carried out as before. The films containing AgAc before and after in situ inversion were investigated by TEM. Since silver salt can be easily reduced to nanoparticles by electron beams of TEM, we obtained silver nanoparticles selectively formed in the P4VP domain that was the isolated core before inversion and the continuous matrix after inversion, as shown in Figure 3. This result implies that silver salt was selectively located in the P4VP domain and effectively moved together with the P4VP block during the inversion. Therefore, by simple treatment with a selective solvent for the core block, it was possible to change the location of silver nanoparticles from isolated islands to a continuous matrix, which may result in a complete change of physical properties such as conductivity. This methodology can be applicable to a variety of nanoparticles as long as their precursors can be coordinated to the P4VP block. However, if P4VP blocks were quaternized by precursors such as $HAuCl_4$,[11,13,14] in situ core−corona inversion was not induced because of strong interactions of quaternized P4VP cores.

In conclusion, films of two-dimensionally compacted micelles of diblock copolymers were successfully fabricated by simple spin coating. Such a film was free-standing without a supporting substrate due to high interaction between coronas of micelles; so that it can be transferable to various substrates and be stacked by multiple transferring. Therefore, we demonstrated a transferable nanopattern from a micellar monolayer of a kinetically frozen self-assembly without a prolonged annealing process. In addition, core−corona inversion of micelles was induced in situ in a free-standing film by a selective solvent for the core without a change of micellar packing. Thus, it was possible to switch nanopatterns between positive and negative tones. As an example, the location of silver nanoparticles was changed from isolated islands to a continuous matrix by in situ core−corona inversion of micelles containing nanoparticle precursors in one of the blocks.

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